

# RESTRICTED MASS TRANSPORT EFFECTS ON THE PYROLYSIS PATHWAYS FOR LIGNIN MODEL COMPOUNDS. ARYL ETHER LINKAGES

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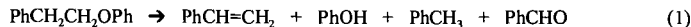
## ABSTRACT

Aryl ethers are important linking units in the structure of lignins and low rank coals that are thermally labile at 375°C. Mass transport limitations experienced in these cross-linked macromolecular solids can lead to alterations in thermochemical processing kinetics and product yields. The molecular level details of these alterations on reaction pathways are revealed through studies of model compounds that are constrained to an inert silica surface through covalent attachments. The thermolysis mechanisms for the silica-immobilized ( $\approx$ )  $\beta$ -aryl ether model compounds,  $\approx\text{PhCH}_2\text{CH}_2\text{OPh}$ ,  $\approx\text{PhOCH}_2\text{CH}_2\text{Ph}$ ,  $\approx\text{PhCH}_2\text{CH}_2\text{OPh-}o\text{-OCH}_3$ , and the  $\alpha$ -aryl ether model,  $\approx\text{PhOCH}_2\text{Ph}$ , have been investigated at 275-375°C. Free-radical rearrangement pathways involving O,C-phenyl shifts are found to be significant for these aryl ethers under diffusional constraints leading to new, unpredicted pyrolysis products. The selectivity for these rearrangement pathways depends strongly on the structure of neighboring molecules, as determined from studies of two-component surfaces containing spacer molecules.

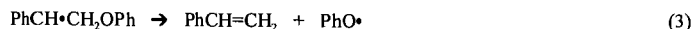
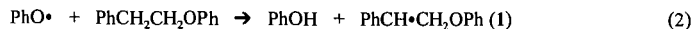
## INTRODUCTION

Lignin is a complex, heterogeneous, three-dimensional biopolymer formed from the enzyme-initiated, dehydrogenative, free-radical co-polymerization of *trans-p*-coumaryl alcohol, *trans*-coniferyl alcohol, and *trans*-sinapyl alcohol.<sup>(1)</sup> Although there are several different types of linkages between monomer units, aryl ether linkages are dominant. In particular,  $\beta$ -aryl ether linkages, as typified by the simplest model compound, phenethyl phenyl ether ( $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OC}_6\text{H}_5$  or PPE), can account for up to half of the total number of linkages. In addition,  $\alpha$ -aryl ether linkages, as typified by the simplest model compound, benzyl phenyl ether ( $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$  or BPE), can account for another 6-8 % of the linkages. The  $\beta$ -aryl ether linkages are typically less reactive thermochemically, since the C-O bond in PPE (ca. 63 kcal mol<sup>-1</sup>) is about 11 kcal mol<sup>-1</sup> stronger than in BPE (ca. 52 kcal mol<sup>-1</sup>).<sup>(2)</sup> However, pyrolysis products and rates can not be easily predicted based solely on bond strength arguments.

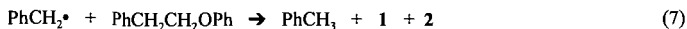
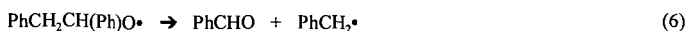
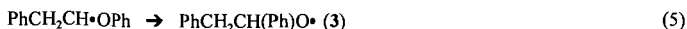
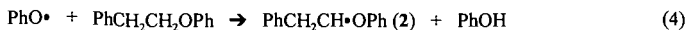
For example, in our earlier study of the pyrolysis of PPE in the liquid and vapor phases at 330-425°C,<sup>(2)</sup> four major products were found (Eq. 1), and an activation energy of only 46 kcal mol<sup>-1</sup> was measured. We showed that the expected phenol and styrene products were formed



by a free radical chain process (propagation steps shown in Eqs. 2-3) following initial C-O homolysis. Even more striking was the discovery of a second previously unreported reaction



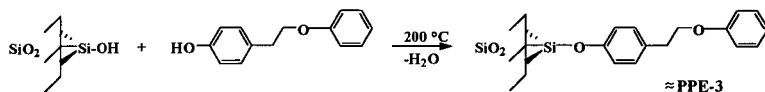
pathway that produced toluene and benzaldehyde in significant yields. This path (Eqs. 4-7), which accounted for typically 25 % of the pyrolysis products, involved the key rearrangement step 5, a 1,2-phenyl shift from oxygen to carbon (neophyl-like rearrangement) in radical intermediate, 2, followed by  $\beta$ -scission of the rearranged radical, 3 (Eq. 6). The selectivity for these two competing pathways, which cycle through the  $\alpha$ -carbon radical (1) and the  $\beta$ -carbon radical (2) was found to be  $3.1 \pm 0.1$  independent of extent of reaction or initial PPE concentration.



We have been exploring in detail the effects of restricted mass transport on pyrolysis reaction mechanisms for a variety of fossil and biomass model compounds.<sup>(3)</sup> Mass transport limitations are known to impact the global kinetics and product yields and distribution in the thermochemical processing of fossil and renewable organic energy resources.<sup>(4)</sup> In our studies, restricted mass transport has been simulated through covalent attachment of the model compounds to a silica surface by means of a thermally robust Si-O-C<sub>aryl</sub> linkage. This research has uncovered numerous examples where product selectivities and reaction rates are significantly altered compared with corresponding fluid phase models. In particular, retrogressive rearrangement and cyclization pathways can be promoted under restricted mass transport conditions. We have now examined several silica-immobilized ( $\approx$ ) model compounds containing the  $\beta$ -aryl ether linkage,  $\approx\text{PhCH}_2\text{CH}_2\text{OPh}$  ( $\approx\text{PPE-3}$ ),  $\approx\text{PhOCH}_2\text{CH}_2\text{Ph}$  ( $\approx\text{PPE-1}$ ),  $\approx\text{PhCH}_2\text{CH}_2\text{OPh-}o\text{-OCH}_3$  ( $\approx\text{PPE-3-}o\text{-OMe}$ ) to see the effect of diffusional constraints on the selectivity for the new reaction path involving rearrangement step 5. Furthermore, we have examined the pyrolysis of a model of the  $\alpha$ -aryl ether linkage,  $\approx\text{PhOCH}_2\text{Ph}$  ( $\approx\text{BPE}$ ), and discovered that an analogous 1,2-phenyl shift occurs leading to new products not reported in fluid phases. The influence of the structure of neighboring molecules on the selectivity for these rearrangement pathways has been examined through the use of two component surfaces containing spacer molecules of varying structure.

## EXPERIMENTAL

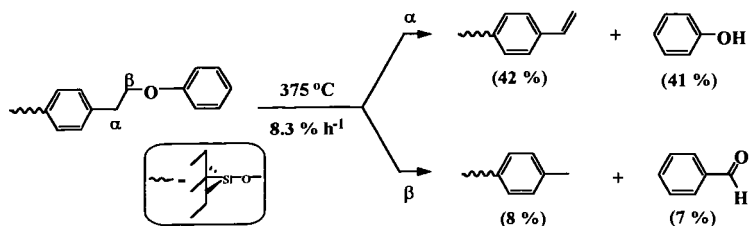
Preparation of the silica-immobilized model compounds involved condensation of phenolic precursors with the surface silanol groups on a fumed silica as shown below for the case of  $\approx\text{PPE-3}$ . The syntheses of the precursor phenols, *p*-HOPhCH<sub>2</sub>CH<sub>2</sub>OPh,<sup>(5)</sup> *p*-HOPhOCH<sub>2</sub>CH<sub>2</sub>Ph,<sup>(5)</sup> *p*-HOPhCH<sub>2</sub>CH<sub>2</sub>OPh-*o*-OCH<sub>3</sub>,<sup>(5)</sup> and *m*-HOPhOCH<sub>2</sub>Ph<sup>(6)</sup> have been previously reported. The general methods for attachment of the phenols to the silica surface (200 m<sup>2</sup> g<sup>-1</sup>; 12 nm primary particle size) have also been described.<sup>(4-6)</sup> Two component surfaces containing an ether model compound and a spacer compound such as biphenyl ( $\approx\text{BP}$ ), naphthalene ( $\approx\text{NAP}$ ), diphenylmethane ( $\approx\text{DPM}$ ), or tetralin ( $\approx\text{TET}$ ) were prepared analogously by co-attachment of the appropriate phenols in a single step.



Thermolyses were conducted in sealed, evacuated ( $2 \times 10^{-6}$  torr) T-shaped Pyrex tubes in a temperature controlled ( $\pm 1^\circ\text{C}$ ) furnace.<sup>(4-6)</sup> Volatile products were collected as they were produced in a liquid nitrogen cold trap, and subsequently analyzed by GC and GC-MS with the use of internal calibration standards. Surface-attached products were similarly analyzed after digestion of the silica in aqueous base, neutralization, extraction of the products into an organic solvent, and silylation of the resulting phenols to the corresponding trimethylsilyl ethers.

## RESULTS AND DISCUSSION

**Phenethyl Phenyl Ether Models.** Pyrolysis of  $\approx\text{PPE-3}$  (0.56 mmol g<sup>-1</sup>) at 375°C generates a set of products comparable to that found for PPE in the liquid and gas phases as shown below. Both reaction pathways, cycling through radicals at the  $\alpha$ - and  $\beta$ -carbons, are found to be operative under restricted mass transport conditions. The measured  $\alpha/\beta$  path selectivity value is 5, which is slightly higher than for fluid-phase PPE as a consequence of the *p*-silyloxy linkage to the surface that stabilizes the  $\alpha$ -radical. This was confirmed by pyrolysis studies of *p*-(CH<sub>3</sub>)<sub>3</sub>SiOPhCH<sub>2</sub>CH<sub>2</sub>OPh (as a model for  $\approx\text{PPE-3}$ ) in the gas phase at 375°C, which



gave a comparable  $\alpha/\beta$  selectivity value of  $4.4 \pm 0.5$ . Furthermore, pyrolysis of the isomeric  $\approx$ PPE-1 ( $\approx$ PhOCH<sub>2</sub>CH<sub>2</sub>Ph; 0.50 mmol g<sup>-1</sup>), where the silyloxy substituent is remote from the  $\alpha$ - and  $\beta$ -carbons, results in a selectivity value of  $3.1 \pm 0.3$  consistent with the removal of the substituent effect.

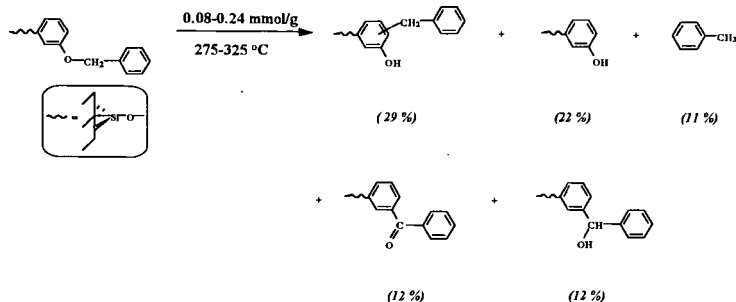
Pyrolysis of  $\approx$ PhCH<sub>2</sub>CH<sub>2</sub>OPh-*o*-OCH<sub>3</sub> ( $\approx$ PPE-3-*o*-OMe; 0.55 mmol g<sup>-1</sup>) was also investigated since this model compound contains the guaiacyl unit that is prominent in lignins from gymnosperms. A comparable product slate to that shown above for  $\approx$ PPE-3 is obtained with an  $\alpha/\beta$  path selectivity of ca. 6. It is clear from the pyrolysis of these three model compounds that the new rearrangement/ $\beta$ -scission path observed for fluid phase PPE is also important under conditions of restricted diffusion.

An examination of the pyrolysis of  $\approx$ PPE-3 in the presence of aromatic spacer molecules reveals that the  $\alpha/\beta$  path selectivity is sensitive to the presence and structure of neighboring aromatic molecules on the surface. This effect was not observed for the pyrolysis of PPE in fluid

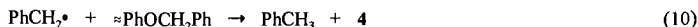
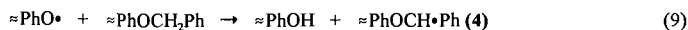
Surface:	$\approx$ PPE-3 / $\approx$ <i>p</i> -BP	$\approx$ PPE-3 / $\approx$ <i>m</i> -BP	$\approx$ PPE-3 / $\approx$ NAP
Coverage: (mmol/g)	0.050 / 0.54	0.066 / 0.51	0.072 / 0.45
$\alpha/\beta$ Selectivity:	$20 \pm 4$	$10 \pm 2$	$20 \pm 2$

phases<sup>(2)</sup> where the path selectivity was independent of the presence of added biphenyl up to the maximum dilution investigated (90% biphenyl). Since the relative rates of hydrogen abstraction from the  $\alpha$ - and  $\beta$ -carbons should not be significantly impacted by the aromatic spacers, our current hypothesis is that the proximate aromatic spacers must be sterically hindering the 1,2-phenyl shift from oxygen to carbon. As illustrated from comparison of the *p*-BP and *m*-BP cases, the degree to which this pathway is hindered will also depend on the orientation and packing efficiency for the molecules on the surface. The effects of spacer structure on the pyrolysis path selectivity for  $\approx$ PPE-3 will continue to be investigated.

**Benzyl Phenyl Ether Model.** Pyrolysis of  $\approx$ BPE generated a more complex product mixture than observed for BPE in fluid phases.<sup>(6)</sup> Although numerous products have been identified, the major products shown below typically account for > 85 mol % of the pyrolysis

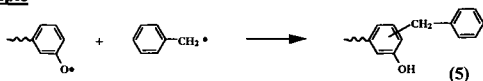


products. As in the case of fluid-phase BPE, the initial event is homolysis of the weak O-C bond as shown in Eq. 8. Arrhenius treatment of 10 pyrolyses ( $0.24 \text{ mmol g}^{-1}$ ) at  $275\text{--}325^\circ\text{C}$  gave  $\log k/s^{-1} = (15.4 \pm 0.6) - (51.0 \pm 1.6)/2.303RT$ . These Arrhenius parameters are in reasonable agreement with the values obtained for pyrolysis of BPE in fluid phases.<sup>(6)</sup> Hydrogen abstraction by the incipient radicals generated the toluene and surface-bound phenol products (Eqs. 9-10).

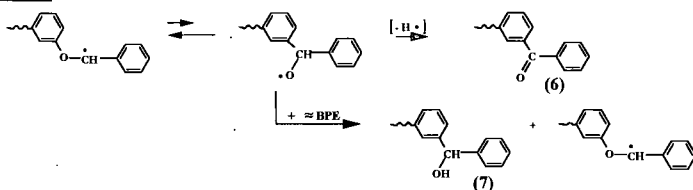


Surprisingly, two additional decomposition routes were found for  $\approx\text{BPE}$  that involved molecular rearrangements that establish a more refractory diphenylmethane-type linkage, as shown below. The first pathway involves recoupling of the radicals formed in step 8 at the ring carbons of the phenoxy radical to form isomers of silica-immobilized benzylphenol (5). This pathway, which accounts for typically 29-37 mol % of the products over a wide range of surface coverages and temperatures is clearly promoted by restricted diffusion compared with fluid phases, where the corresponding products typically account for only 10-15 mol % of the pyrolysis

#### Recouple



#### Phenyl Shift



products. The second rearrangement path, not reported in fluid-phase studies of BPE, forms the surface-bound benzophenone (6) and benzhydrol (7) products. As in the case of the PPE models, a 1,2-phenyl shift from oxygen to carbon occurs to generate an oxy-radical intermediate. In contrast to PPE models, this radical does not possess a competitive  $\beta$ -scission pathway and undergoes hydrogen transfer reactions to generate the ketone and alcohol products.

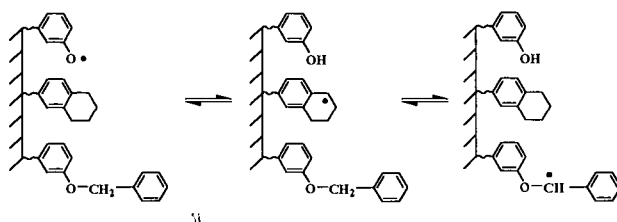
As shown in Table 1, these rearrangement pathways for  $\approx\text{BPE}$  typically account for ca. 50 mol % of the pyrolysis products. However, the path selectivity is found to be very dependent on both surface coverage and the structure of neighboring spacer molecules (tetralin or naphthalene) on the surface. As the surface coverage decreases, the rates of hydrogen transfer steps on the surface decrease as molecules become increasingly separated on the silica surface.

Table 1. Selectivity for Rearrangement Pathways in  $\approx\text{BPE}$  Pyrolysis

surface composition	coverage ( $\text{mmol g}^{-1}$ )	product yield, 5 + 6 + 7, (mol %)	path selectivity, (recouple/phenyl shift), 5 / (6 + 7)
$\approx\text{BPE}$	0.24	$51.9 \pm 1.3$	1.00
	0.18	$50.2 \pm 1.8$	1.34
	0.094	$50.2 \pm 1.5$	1.78
	0.084	$47.3 \pm 1.6$	2.04
$\approx\text{BPE}/\approx\text{TET}$	0.068/0.17	$54.3 \pm 3.0$	1.21
$\approx\text{BPE}/\approx\text{NAP}$	0.067/0.14	$40.7 \pm 2.4$	2.94

This reduces the rate of formation of radical 4, as well as subsequent hydrogen transfer steps, and results in an increased selectivity for the simple recoupling path. This premise is further supported by the effect of spacer structure on the rearrangement path selectivity. The aromatic spacer,

naphthalene ( $\approx$ NAP), serves as a barrier that further retards hydrogen transfer steps and enhances the selectivity for recoupling. On the other hand, the hydroaromatic spacer, tetralin ( $\approx$ TET), is able to participate in a well-established hydrogen transfer, radical relay process (shown below),<sup>(4b,c)</sup> which alleviates some of the diffusional constraints in producing radical **4** by reducing the separation between molecules and hydrogen-abstracting radicals on the surface. This results in a path selectivity comparable to that of  $\approx$ BPE at high surface coverages.



## CONCLUSIONS

Pyrolysis studies of lignin model compounds under restricted mass transport conditions have revealed the significance of new product forming reaction pathways involving 1,2-phenyl shift rearrangements in radical intermediates of the type,  $\approx$ PhCH<sub>2</sub>CH $\cdot$ OPh and  $\approx$ PhCH $\cdot$ OPh. Related rearrangement pathways have been found to be promoted in the pyrolysis of the coal model compounds, silica-immobilized bibenzyl<sup>(4b,c)</sup> and benzyl phenyl sulfide,<sup>(8)</sup> involving  $\approx$ PhCH<sub>2</sub>CH $\cdot$ Ph and  $\approx$ PhSCH $\cdot$ Ph intermediates, respectively. These rearrangement paths are often promoted by diffusional constraints compared with fluid phases, but can be significantly impacted by the proximity and structure of neighboring molecules.

## ACKNOWLEDGMENTS

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## REFERENCES

- (a) Alder, E. J. *Wood Sci. Technol.* **1977**, *11*, 169. (b) Nimz, H. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 313.
- Britt, P. F.; Buchanan, III, A. C.; Malcolm, E. A. *J. Org. Chem.* **1995**, *60*, 6523.
- (a) Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B.; Biggs, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2182. (b) Buchanan, III, A. C.; Dunstan, T. D. J.; Douglas, E. C.; Poutsma, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 7703. (c) Buchanan, III, A. C.; Biggs, C. A. *J. Org. Chem.* **1989**, *54*, 517. (d) Britt, P. F.; Buchanan, III, A. C. *J. Org. Chem.* **1991**, *56*, 6132. (e) Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B. *Energy & Fuels* **1998**, *12*, 649. (f) Britt, P. F.; Buchanan, III, A. C.; Malcolm, E. A.; Biggs, C. A. *J. Anal. Appl. Pyrolysis* **1993**, *25*, 407. (g) Buchanan, III, A. C.; Britt, P. F.; Biggs, C. A. *Energy Fuels* **1990**, *4*, 415.
- (a) Gavalas, G. R. *Coal Pyrolysis*; Elsevier: Amsterdam, 1982. (b) Solomon, P. R.; Fletcher, T. H.; Pugmire, R. J. *Fuel* **1993**, *72*, 587. (c) Suuberg, E. M. in *Chemistry of Coal Conversion*; Schlosberg, R. H., Ed.; Plenum Press: New York, 1985; Chapter 4. (d) Wanzl, W. *Biomass and Bioenergy* **1994**, *7*, 131. (e) Blasi, C. D. *Biomass and Bioenergy* **1994**, *7*, 87. (f) Serio, M. A.; Charpenay, S.; Basilakis, R.; Solomon, P. R. *Biomass and Bioenergy* **1994**, *7*, 107.
- Britt, P. F.; Buchanan, III, A. C.; Thomas, K. B.; Lee, S.-K. *J. Anal. Appl. Pyrolysis* **1995**, *33*, 1.
- (a) Buchanan, III, A. C.; Britt, P. F.; Skeen, J. T.; Struss, J. A.; Elam, C. L. *J. Org. Chem.*, **1999**, in press. (b) Buchanan, III, A. C.; Britt, P. F.; Skeen, J. T. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1997**, *42*, 15.
- Hatcher, P. G. *Org. Geochem.* **1990**, *16*, 1959.
- Ismail, K.; Mitchell, S. C.; Brown, S. D.; Snape, C. E.; Buchanan, III, A. C.; Britt, P. F.; Franco, D. V.; Maes, I. I.; Yperman, J. *Energy & Fuels* **1995**, *9*, 707.